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Influence of AlN layers on the interface stability of HfO_2 gate dielectric stacks

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ABSTRACT

The influence of thick (~ 10 nm) AlN overlayers on the interface structure and reactions in Si gate stacks with HfO_2 dielectrics was investigated. Annealing caused a reduction of the interfacial SiO_2 at the Si interface. At high temperatures (~ 1000 ºC) a silicide reaction was observed at the HfO_2/Si interface. No reactions were observed for stacks processed similarly but with WN or TiN overlayers instead of AlN. The reaction mechanisms, in particular the role of oxygen deficiency of the HfO_2, and the consequences for the electrical properties are discussed.

The continuous scaling of complementary metal-oxide semiconductor (CMOS) devices requires novel gate stacks that include high dielectric constant (*k*) materials, such as HfO_2, and a new metal gate technology [1]. Metal gates offer improved materials compatibility with high-*k* gate stacks and reduce gate depletion effects [2]. An important consideration in the selection of metal gate materials are metal work functions that are suitable for *n*- and *p*-channel devices [2]. In practice, the effective work functions in high-*k* gate stacks are, however, believed to be controlled by the nature of the high-k/metal interface [3] and defects, such as oxygen vacancies in the high-*k* dielectric [4]. Some electrodes, such as Ti, are reactive and cause thinning of SiO_2 layers that are typically present at the interface with Si [5]. Recently, interfacial layers, such as AlN, have attracted attention as means to control the effective metal gate work function [6,7]. In particular, it was found that thin AlN interlayers between a HfO_2 gate dielectric and a TiSiN gate caused a large, advantageous increase in the effective work function from 4.82 eV without AlN to 5.08 eV with AlN [6]. Wurtzite AlN is a dielectric with a relatively high dielectric constant ($k \sim 8.5$ [8]) and large band gap (6.2 eV [9]). HfO_2/AlN interfaces are reported to be thermally stable in nitrogen up to 1500 ºC [10]. The goal of this paper is to investigate the mechanisms by which AlN layers control the electrical properties of high-*k* gate stacks, in particular the observed increase in the effective workfunction [6].

Thick (~ 10 nm) HfO_2 gate dielectric films were grown at 350 °C by atomic layer deposition (ALD) on O_3-cleaned p-Si using tetrakis-ethyl-methyl-amino hafnium as the precursor (100 cycles). A post-high-*k* deposition anneal (PDA) was performed at 700 °C for 60 sec in 30 torr N_2. The HfO_2 stacks were capped with 10 nm AlN. For comparison, stacks with WN or TiN electrodes were also studied. AlN and WN were deposited by reactive sputtering at room temperature from metal targets in nitrogen gas, whereas TiN was deposited by chemical

vapor deposition (CVD). Auger analysis showed that the Al/N ratio was approximately 1:1, indicating near stoichiometric AlN films within the detection limit of the method [6]. All stacks were capped with 5 nm Si deposited by PVD at room temperature (in-situ for WN and AlN stacks). Selected gate stacks were annealed (RTA) for 5 s at 700 °C and 1000 °C in N_2, respectively.

Transmission electron microscopy (TEM) cross-section samples were prepared by standard sample preparation techniques. Conventional high-resolution transmission electron microscopy (HRTEM), high-angle annular dark-field (HAADF) imaging and electron energy loss spectroscopy (EELS) were performed using a field-emission TEM (Tecnai F30U), which was operated at 300 kV. The probe size for EELS was ~ 3 Å and the energy resolution, defined as the full-width at half-maximum (FWHM) of the zero-loss peak was about 0.85 – 0.90 eV. Al $L_{2,3}$-edges (~ 77 eV) were acquired for 5 s, using a probe that was scanned along a 3-nm line parallel to the interfaces. Layer thicknesses were estimated from line intensity profiles across HRTEM images.

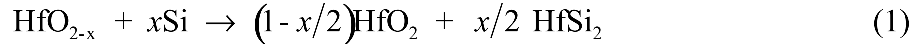
Figure 1a shows a HRTEM image of the as-deposited Si/HfO_2/AlN stack. A thin SiO_2 layer (t_{SiO_2} = 1.23±0.02 nm) was present at the Si substrate interface and the HfO_2 film was polycrystalline as expected due to the 700 ºC PDA. The AlN layer was also polycrystalline with very small grains and electron diffraction confirmed that the grains possessed the wurtzite structure. After the 1000 ºC RTA (Fig. 1b) the interfacial SiO_2 thickness was significantly reduced (t_{SiO_2} = 0.58±0.04 nm). A reduction in interfacial SiO_2 thickness was found to occur also after the 700 ºC RTA (not shown), although it was less severe (t_{SiO_2} = 0.91±0.02 nm). While the Si interface remained smooth after the 700 ºC RTA, reaction was observed at the Si/HfO_2 interface at several locations after the 1000 ºC RTA (Fig. 2). Large (> 20 nm) grains of

a crystalline reaction phase were found to protrude into the Si, accompanied by local thinning of the HfO_2 dielectric (Fig. 2a). The reaction phase was Hf-rich and thus appeared much brighter than the Si substrate in the HAADF images due to their atomic-number sensitive contrast (Fig. 2b). EELS showed that the reaction phase contained no oxygen, and was thus likely a Hf-silicide. No obvious reactions occurred at the HfO_2/AlN interface. In contrast to stacks with AlN layers, WN and TiN stacks annealed at 1000 ºC did not exhibit any detectable thinning of the interfacial SiO_2 or silicide reaction at the interface (Fig. 3).

The fine structure of EELS Al $L_{2,3}$-edges (Fig. 4) was consistent with AlN even after the 1000 ºC RTA [11,12] and did not exhibit features characteristic for either amorphous or crystalline Al_2O_3 [11]. The peak separation of the first two peaks was somewhat reduced similar to oxygen doped AlN [12]. Furthermore, the plasmon peak was shifted in the 1000 ºC annealed sample to higher energy losses. However, in addition to oxygen uptake from the HfO_2, these changes could have been due to surface oxidation of the TEM sample surface [13] as some intensity in the oxygen K-edge was detected even in the sample with no RTA. Furthermore, although high-purity N_2 was used during the RTA, it likely contained sufficient oxygen to oxidize the Si capping layer during the 1000 ºC RTA, and potentially some of the AlN. However, these reactions could not explain the thinning of the interfacial SiO_2 and the silicide reaction, in particular since they were not observed for the WN and TiN electrodes.

The thinning of interfacial SiO_2 and silicide reaction could, however, be explained with oxygen removal from the HfO_2 by the AlN. AlN is known to have a high solubility for oxygen [14,15] which may also have been promoted additionally by some degree of N-deficiency. As HfO_2 is thermodynamically more stable than SiO_2, oxygen deficiency would initially be compensated by reduction of the interfacial SiO_2 [16], which was consistent with the observed

thinning. In areas along the interface where all of the SiO_2 was consumed, a direct HfO_2/Si interface would be formed. While stoichiometric HfO_2 in contact with Si was expected to be thermodynamically stable, silicide reactions at direct HfO_2/Si interfaces are known to be driven by O-deficiency in the high-*k* [16,17]. For example (in case of disilicide formation) the following reaction may have a negative free energy change, as shown elsewhere [16]:



$$HfO_{2-x} + x\mathrm{Si} \rightarrow (1 - x/2)HfO_2 + x/2\ HfSi_2 \qquad (1)$$

where x indicates the degree of oxygen deficiency of the HfO_2. The results also established that the silicide reaction did not involve a gas phase, such as SiO, as frequently proposed in the literature (for references see [16]), because the stacks were capped with Si.

In addition to the formation of Al-O bonds [6], the observed changes in the effective work function [6] by use of AlN layers could have been related to the creation of oxygen vacancies in the dielectric. No silicide reaction was observed for the much thinner AlN layers employed in the gate stacks investigated in ref. [6]; thus oxygen deficiency in the high-*k* and reaction at the Si interface can likely be controlled by the precise annealing conditions and the thickness of the AlN layer.

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FIGURE CAPTIONS

Figure 1

HRTEM images of the Si/AlN/HfO_2/Si gate stack (a) as-deposited and (b) after 1000 °C RTA. Note the thickness reduction of the SiO_2-like layer at the Si interface in (b). In addition to SiO_2 thinning, silicide reaction was observed (see Fig. 2).

Figure 2 (color online)

Interface reaction observed for the Si/AlN/HfO_2/Si gate stack after the 1000 °C RTA: (a) HRTEM image showing HfO_2 thinning (arrows) near the reaction phase at the Si interface. (b) HAADF image showing Hf-rich silicide reaction phase protruding into the Si substrate. The inset shows the crystalline silicide.

Figure 3

HRTEM images of (a) the Si/WN/HfO_2/Si stack after RTA at 1000 °C and (b) the Si/TiN/HfO_2/Si stack after RTA at 1000 °C, showing no SiO_2 thinning and a stable interface with the Si substrate.

Figure 4 (color online)

Al $L_{2,3}$-edge EELS of the AlN layer after the 1000 °C RTA.

(a)

AlN HfO_2 Si

5 nm

(b)

AlN HfO_2 Si

5 nm

(a)
AlN
Si
10 nm
(b)
AlN
Si
5 nm

(a)

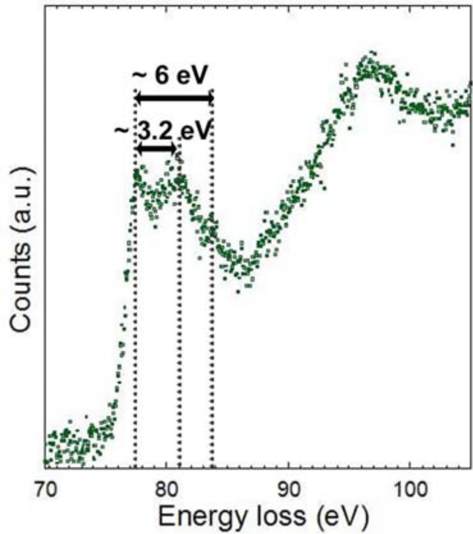
WN HfO_2 Si

5 nm

(b)

TiN HfO_2 Si

5 nm



~ 6 eV
~ 3.2 eV
Counts (a.u.)
70
80
90
100
Energy loss (eV)